Synthesis of ABCD-Type Miktoarm Star Copolymers and Transformation into Zwitterionic Star Copolymers

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Received 28 March 2007; accepted 26 May 2007
DOI: 10.1002/pola.22229
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: ABCD-type 4-miktoarm star copolymers of styrene (St), \(\alpha\)-methylstyrene (\(\alpha\)MSt), tert-butyl methacrylate (tBuMA), and 4-vinylpyridine (4VP) were synthesized via anionic polymerization using 1,3-bis(1-phenylvinyl)benzene (m-DDPE) as the linking molecule. The synthetic route was rationally designed with respect to the reactivity of individual propagating anion towards the double bond of m-DDPE. Thus the synthesis includes several consecutive key reactions, for example, the monoaddition of polystyryllithium towards m-DDPE, the polymerization of tBuMA initiated by the resulting monoadduct to produce a diblock macromonomer, the coupling of the macromonomer with poly(\(\alpha\)-methylstyryl)lithium to form a 3-arm star anion, and the polymerization of 4-vinylpyridine initiated by the star anion. These reactions were conducted either in a one-pot process, in which the diblock macromonomer was \textit{in situ} coupled with poly(\(\alpha\)-methylstyryl)lithium, or in a batch polymerization process, in which the same diblock macromonomer was separated. The final product was hydrolyzed to produce a zwitterionic miktoarm star copolymer, which was soluble at lower pH but insoluble in neutral and basic solution.

Keywords: anionic polymerization; hydrolysis; living polymerization; star copolymers; star polymer; zwitterionic polymers

INTRODUCTION

The synthesis of well-defined polymers with nonlinear topologies by anionic polymerization has received much attention in recent years.\(^1\)\(^-\)\(^5\) A diversity of polymers with well-defined complex structures, such as star,\(^6\)\(^-\)\(^10\) graft,\(^11\) dendritic\(^12,13\) polymers, have been synthesized using mostly chlorosilane titration and diphenylethylene (DPE) chemistry. Nonetheless, the synthesis of ABCD-type 4-miktoarm star copolymer is still a challenge due to the stringent polymerization conditions. Up to date there are only four papers in the literature describing the synthesis of ABCD-type star quaternary copolymers. In 1993, Hadjichristidis and Iatrou\(^14\) prepared miktoarm star copolymer of styrene, isoprene, butadiene, and 4-methylstyrene using tetrachlorosilane as the linking agent. The synthesis involved step-by-step coupling of polymer anions with SiCl\(_4\) and the subsequent macromolecular linking agent. However, the reaction was very time-consuming due to the steric hindrance of
the di- and tri-functionalized linking agents. Recently, the same research group\textsuperscript{15} combined the advantages of chlorosilane coupling and DPE chemistry into a single compound, 4-(dichloromethylsilyl) diphenylethylene, which was used successfully in the synthesis of a miktoarm star quaternary copolymer of styrene, isoprene, examethylcyclosiloxane (D\textsubscript{3}), and 2-vinylpyridine. Hirao and Higashihara\textsuperscript{16} used 1,1-bis(3-chloromethylphenyl)ethylenylene, a compound synthesized in their own laboratory, to prepare miktoarm copolymers composed of polyisoprene, polystyrene, polymethoxystyrene, and poly(4-trimethylsilylethylene). Later they designed and synthesized an asymmetric DPE derivative, 1-(3-\textit{tert}-butylidimethylsilyloxymethylphenyl)-1-phenylethylene, and used it in the synthesis of ABCD-type star copolymer of styrene, \textit{z}-methylstyrene, 4-methylstyrene, and methyl methacrylate through iterative coupling and transformation reactions.\textsuperscript{17}

Bifunctional DPE derivatives, such as 1,3-bis(1-phenylnvinyl)benzene (\textit{m}-DDPE), were widely used in macromolecular engineering by anionic polymerization.\textsuperscript{18} Quirk and Yoo synthesized 3-functionalized linking agent.\textsuperscript{19} In a previous paper, we reported the synthesis of ABC-type miktoarm star copolymer of styrene, isoprene, and 1,3-cyclohexadiene (CHD) through a modified \textit{m}-DDPE route depending on monomers.\textsuperscript{20} The key steps to the success of ABC miktoarm structure are the exclusive mono-addition of polystyryllithium towards \textit{m}-DDPE to form a macronomer, the stoichiometric coupling of the resulting macronomer with polyisoprene, as well as the efficient initiation of the third monomer, CHD, with the aid of an isoprene “seeding” process.

In the present work, we synthesize ABCD-type miktoarm star copolymers through a one-pot continuous polymerization process, which is much simpler than the conventional batch reaction process. Among various linking molecules, we prefer \textit{m}-DDPE because of its easy preparation and handling as well as relatively shorter reaction time. Nevertheless, the synthesis of ABCD-type stars using \textit{m}-DDPE is much more complicated than that of ABC stars due to higher selectivity of various anion species for different monomers. In addition, the reactivity of the double bond of \textit{m}-DDPE depends on the nature of anions. For example, (poly)alkyllithium such as butyllithium or polystyryllithium reacts readily with the double bond of \textit{m}-DDPE, while polymethacrylylithium does not. Taking all these factors into account, we choose styrene, \textit{z}-methylstyrene (\textit{z}MSt), \textit{tert}-butyl methacrylate (\textit{t}BuMA), and 4-vinylpyridine (4VP) as monomers. Thus, polystyryllithium adds to equivalent amount of \textit{m}-DDPE to form a mono-adduct, which then initiate polymerization of \textit{t}BuMA to produce a diblock macromonomer. The macronomer couples, either in situ or after separation, with poly(\textit{z}-methylstyrlyl)lithium to form an ABC-star anion which initiates the polymerization of 4VP (Scheme 1) to yield the target product. With this rationally designed process, we are able to conduct the synthesis in the same flask with no necessary of terminating the intermediate species (the one-pot process).

The product can be used as a precursor for miktoarm star polymers with zwitterionic segments. Zwitterionic polymers are an important class of functional polymers that have a variety of applications.\textsuperscript{21} A number of linear block copolymers containing zwitterionic segments were synthesized through anionic polymerization,\textsuperscript{22–27} group transmission polymerization (GTP),\textsuperscript{28,29} atom transfer radical polymerization (ATRP),\textsuperscript{30,31} and polymer reaction.\textsuperscript{32–34} Nonetheless, the report on star-like zwitterionic copolymers is scarce. Armes and Cai synthesized a Y-shaped zwitterionic block copolymers (\textit{AB}_{2}) through ATRP using a trifunctional initiator.\textsuperscript{35} The synthesis of ABCD-type miktoarm zwitterionic star copolymer has never been reported.

**EXPERIMENTAL**

**Materials**

Styrene (National Pharmaceutical (NP), \textgeq 99%), \textit{z}-methylstyrene (NP, \textgeq 99%), \textit{tert}-butyl methacrylate (\textit{t}-BuMA, TCI, 96%), and 4-vinylpyridine (4VP, Alfa Aesar, 96%) were stirred over CaH\textsubscript{2} overnight, distilled and stored under nitrogen atmosphere at 4 °C. These monomers were redistilled over di-n-butylmagnesium (MgBu\textsubscript{2}) (Aldrich, 1.0 M in heptane), \textit{n}-butyllithium (n-BuLi) (Fluka, 2.5 M in heptane), and tri-n-octylaluminium (0.3 M solution in heptane, for \textit{t}-BuMA and 4VP), respectively, prior to use. sec-Butyllithium(\textit{sec}-BuLi) (Acros, solution in cyclohexane/heptane) and methyl lithium (Acros, 1.6 M solution in diethyl ether) were used as received. The concentration of sec-BuLi was analyzed by double titration. Cyclohexane (Shanghai
Feida, 99.5%) and tetrahydrofuran (THF) (Shanghai Feida, 99.5%) were refluxed over sodium (Na) in the presence of benzophenone until a purple color was attained. These solvents were redistilled over 1,1-diphenylhexyllithium (DPELi, adduct of n-BuLi or sec-BuLi and DPE) or polystyryllithium (PSLi) in vacuum line before use. Methyltriphenylphosphonium bromide (Lancaster, >98%) and 1,3-dibenzoylbenzene (Aldrich, 98%) were vacuum dried at 50 °C for 12 h. 1,3-bis(1-phenylvinyl)benzene (m-DDPE) was synthesized from 1,3-dibenzoylbenzene via the Wittig reaction of methyltriphenylphosphonium bromide and methylithium in ether according to a previous procedure.20 Clear oil: yield 40%; Purity 98.2% by HPLC.

**1H NMR (CDCl3):** δ (ppm) = 7.37–7.27 (m, 14 H, aromatic), 5.47 (m, 4 H, =CH2). GC–MS: C, 93.6%; H, 6.4%. Found: C, 93.0%; H, 6.5%.

**FTIR (NaCl):** ν = 3080 cm⁻¹ (=CH2), 1610 cm⁻¹ and 1493 cm⁻¹ (aromatic ring). UV–vis (cyclohexane): λmax (by second derivative) = 223, 234, 252, 258, 264, 267, 271, 284, 292 nm.

### Synthesis of 4-Miktoarm Star Copolymer

All of the reactions were performed in round-bottom flasks connected to the vacuum line. The glass apparatus were dried by three times of flaming/N₂-purging/evacuating, and rinsed successively with dilute solution of sec-BuLi (one time) and dry cyclohexane (three times) before polymerization. All reactions were conducted in an inert atmosphere.

### One-Pot Method

Cyclohexane (30 mL) and styrene (1.82 g, 17.48 mmol) were distilled over PSLi and MgBu₂, respectively, into the reaction flask. sec-BuLi (0.22 mmol, 0.20 mL of cyclohexane/heptane solution) was injected into the system using a syringe. Upon the addition of initiator the color of the solution turned light orange indicating the initiation of the polymerization. The reaction mixture was thermostated at 40 °C for 2 h. The resulting polystyryllithium solution was slowly dropped into a solution of m-DDPE (0.06 g, 0.22 mmol) in THF (100 mL) with vigorous stirring at −78 °C (dry ice/acetone bath). The solution immediately became dark red in color indicating the addition reaction of polystyryllithium to m-DDPE. After 3 h an aliquot of mixture (PSDDPE) was taken for analysis. The second monomer, t-BuMA (1.64 g, 11.51 mmol) was charged into the reaction mixture. The dark red color of the solution changed into light yellowish color indicative of the polymerization of t-BuMA. The reaction mixture was stirred for another 1 h at

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about -40°C. An aliquot of the mixture was taken for analysis. Characterization results: GPC: PS-DDPE: $M_n$GPC = $8 \times 10^3$ g/mol, $M_w$/
$M_n$ = 1.11, $M_n$ theo. = $8.3 \times 10^3$ g/mol; Diblock macromonomer (PSDDPE-PrBuMA): $M_n$GPC = 14.7
$\times 10^3$ g/mol, $M_w$/
$M_n$ = 1.25; PrBuMA: $M_n$NMR
$= 7.2 \times 10^3$ g/mol, $M_n$theo. = 7.5 $\times 10^3$ g/mol.

Poly($z$-methylstyryl)lithium (PzMStLi) was prepared by sec-BuLi (0.22 mmol, 0.20 mL of cyclohexane/heptane solution) in THF (70 mL) (P
a
StLi) was prepared by sec-BuLi (0.22 mmol, 0.20 mL of cyclohexane/

Hydrolysis of Four-Arm Star Polymer

The 4-arm product (0.11 g) of one-pot method was dissolved in 10 mL of 1,4-dioxane (resulted in slight blue transparent solution) in the presence of HCl (0.6 mL concentrated HCl). The solution was refluxed at 85 °C for 8–10 h. The resulting blue milky solution was dropped into large excess of n-hexane for the precipitation of the product. The obtained white powder was washed with n-hexane ($\geq$99.0%) and deionized water, then vacuum dried at 40 °C for several days.

The product obtained after hydrolysis was dissolved in mixed solvent of THF and H2O (1/1, v/v) to form a transparent solution. The solution was then titrated with 0.20 M NaOH solution while the process was monitored by a digital pH meter and the transmittance of the solution was measured by UV–vis spectrometry (working wavelength 600 nm).

**Characterization**

High performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (SymmetryShieldB\textsuperscript{TM} RP-18, 5.0 μm, 4.6 × 250 mm), and a UV-detector (254 nm). Acetonitrile/water (83/17, v/v) was used as eluent (1.0 mL min \textsuperscript{-1}) at 40 °C. $^1$H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl\textsubscript{3} or THF-d\textsubscript{6}/D\textsubscript{2}O (v/v 1/3, for hydrolyzed product) as the solvent and tetramethylsilane as the reference. Gas Chromatography/Mass Spectroscopy (GC–MS) was performed on a Finnigan Voyager
instrument in electrospray ionization mode (70 eV). Fourier transform infrared spectroscopy (FTIR) was performed on a Magna-550 instrument (sodium chloride pellet). The ultraviolet absorption of m-DDPE in cyclohexane was recorded by a Perkin–Elmer Lambda 35 UV–vis spectroscope at 25 ± 0.1 °C with scanning wavelength from 190 to 600 nm. Potentiometric measurement was carried out with a digital 620/640 pH-meter (Shanghai Yingge instrument). Elemental analysis was carried on Elementar Vario EL Instrument. The number–average molecular weight, $M_n$, and polydispersity index, $M_w/M_n$, of all samples were measured by gel permeation chromatography (GPC) through three Waters Styrage columns (pore size: $10^2$, $10^3$, and $10^4$ Å) in series calibrated by narrow polystyrene standard with molecular weight ranging from $2.2 \times 10^5$ to $5.15 \times 10^5$ g/mol. THF was used as the eluent at a flow rate of 1.0 mL·min$^{-1}$ at 40 °C. The elution of the sample was detected by a Waters 410 RI detector. The mass spectrum of polymers was acquired using a Voyager DE–STR matrix assisted laser desorption/ionization time of flight (MALDI-TOF MS) mass spectrometer equipped with a 337 nm nitrogen laser. Samples, dithanol (matrix) and silver trifluoroacetate were dissolved in THF with the concentrations of 10, 20, and 10 mg/mL, respectively. These solutions were mixed in the volume ratio of matrix/polymer/salt = 10/2/1. A volume of 0.5 µL of the mixed solution was placed on a copper plate and air-dried at ambient temperature. Mass spectra were acquired in positive linear mode using an acceleration voltage of 25 kV. External mass calibration was performed using a standard peptide mixture (insulin, thioredoxin). Spectra were obtained by setting the laser power close to the threshold of ionization and generally 700 pulses were acquired and averaged.

RESULTS AND DISCUSSION

The synthetic route of the 4-miktoarm ABCD-type star copolymers, in which A is polystyrene (PS), B poly(tert-butyl methacrylate) (PtBuMA), C poly(z-methylstyrene) (PzMSt), and D poly(4-vinylpyridine) (P4VP), is outlined in Scheme 1. The synthesis involves a diblock macromonomer process, PSDDPE-b-PtBuMA, and is quite selective in polymerization sequences. Since the propagating anions of PtBuMA lack ability of addition towards double bond of m-DDPE, these arms are always chosen to be polymerized by the initiation of a preceding arm. Thus, polystyrene is prepared as the first arm, followed by monoaddition towards m-DDPE. The monoadduct is used in situ to initiate the polymerization of t-BuMA. The resulting copolymer, PSDDPE-b-PtBuMA, carrying an anion terminus and a DDPE double bond at its center, is a diblock macromonomer which is capable of further coupling in situ (in one-pot approach) or after termination (in batch approach) with poly(z-methylstyryl)lithium to produce a three arm star copolymer. The resulting DDPE anion formed in the coupling reaction can initiate the polymerization of vinylpyridine to prepare the target ABCD miktoarm star copolymer, (PS)(PtBuMA)(PzMSt)(P4VP).

Synthesis of ABCD-Type Miktoarm Star Copolymer, (PS)(PtBuMA)(PzMSt)(P4VP)

Synthesis of the Diblock Macromonomer, PSDDPE-b-PtBuMA

A key step in the synthesis of the diblock macromonomer is the control of monoaddition of poly(styryllithium) towards m-DDPE. The addition reaction formed diadduct in nonpolar solvents but monoadduct in polar solvents such as THF, or mixture of THF and cyclohexane, using large excess of m-DDPE. McGrath and coworkers mentioned, without detailed results, that monoadduct was predominant even for stoichiometric amount of butyllithium and m-DDPE in THF. In a previous report, we synthesized the monoadduct using fourfold excess of m-DDPE in THF/cyclohexane (v/v = 3/1). In the present work, the feed amount of m-DDPE is reduced to be equivalent to lithium. Yet the functionality of the product is still very high as analyzed by GPC, 1H-NMR, and MALDI-TOF MS (see Supporting Information).

The resulting monoadduct is used in situ to initiate the polymerization of tBuMA at approximately −40 °C. The polymerization is indicated by the color change of the reaction solution from dark red to pale yellow. The remaining double bond of m-DDPE moiety is dormant due to the weak nucleophilicity of the propagating anion during tBuMA polymerization. Thus the product should be a diblock macromonomer, carrying a DDPE double bond at its linking point. An aliquot of the reaction mixture is terminated by methanol and the mixture is analyzed by
Figure 1. Gel permeation chromatograms (GPC) monitoring synthesis of 4-miktoarm star block copolymer of styrene (St), \(\alpha\)-methylstyrene (\(\alpha\)MSt), \(\alpha\)-tert-butyl methacrylate (tBuMA), and 4-vinylpyridine (4VP). (I) one-pot method (no. 3, Table 1): (a) monoadduct (PS-DDPE): styrene: 1.82 g, 17.48 mmol; sec-BuLi: 0.22 mmol; 1,3-bis(l-phenylvinyl)benzene (\(m\)-DDPE): 0.061 g, 0.22 mmol; Temp.: \(-78^\circ\) C. (b) PSDDPE-b-PtBuMA: tBuMA: 1.64 g, 11.51 mmol, initiated by the monoadduct at \(-49^\circ\) C. (c) Poly(\(\alpha\)-methylstyryl)lithium (P\(\alpha\)MStLi): \(\alpha\)-methylstyrene: 1.82 g, 15.40 mmol; sec-BuLi: 0.22 mmol; Temp.: \(-78^\circ\) C. (d) 3-Miktoarm star polymer: coupling product of P\(\alpha\)MStLi and PSDDPE-PtBuMA at \(-78^\circ\) C in THF for 3–4 h. (e) 4-Miktoarm star polymer: 4-vinylpyridine: 1.76 g, 16.96 mmol initiated by 3-miktoarm anion; Temp.: \(-78^\circ\) C. (II) Batch approach (no. 4, Table 1): all the procedure and the condition are the same with the one-pot method except that the diblock macromonomer PSDDPE-b-PtBuMA was purified. (III) Final product before and after purification with cyclohexane.

The \(M_n\) of PS-DDPE is measured by GPC calibrated with narrow standard polystyrene. The \(M_n\) of PtBuMA arm is calculated from the integration ratio of aromatic and methyl protons in NMR spectrum. The calculated \(M_n\) of PtBuMA (\(M_n\)NMR = 7.2 \(\times\) 10^3 g/mol) is in good agreement with the theoretical value (\(M_n\) theor. = 7.5 \(\times\) 10^3 g/mol), for example, the feed ratio of monomer to initiator.

**Figure 1.** Gel permeation chromatograms (GPC) monitoring synthesis of 4-miktoarm star block copolymer of styrene (St), \(\alpha\)-methylstyrene (\(\alpha\)MSt), \(\alpha\)-tert-butyl methacrylate (tBuMA), and 4-vinylpyridine (4VP). (I) one-pot method (no. 3, Table 1): (a) monoadduct (PS-DDPE): styrene: 1.82 g, 17.48 mmol; sec-BuLi: 0.22 mmol; 1,3-bis(l-phenylvinyl)benzene (\(m\)-DDPE): 0.061 g, 0.22 mmol; Temp.: \(-78^\circ\) C. (b) PSDDPE-b-PtBuMA: tBuMA: 1.64 g, 11.51 mmol, initiated by the monoadduct at \(-49^\circ\) C. (c) Poly(\(\alpha\)-methylstyryl)lithium (P\(\alpha\)MStLi): \(\alpha\)-methylstyrene: 1.82 g, 15.40 mmol; sec-BuLi: 0.22 mmol; Temp.: \(-78^\circ\) C. (d) 3-Miktoarm star polymer: coupling product of P\(\alpha\)MStLi and PSDDPE-PtBuMA at \(-78^\circ\) C in THF for 3–4 h. (e) 4-Miktoarm star polymer: 4-vinylpyridine: 1.76 g, 16.96 mmol initiated by 3-miktoarm anion; Temp.: \(-78^\circ\) C. (II) Batch approach (no. 4, Table 1): all the procedure and the condition are the same with the one-pot method except that the diblock macromonomer PSDDPE-b-PtBuMA was purified. (III) Final product before and after purification with cyclohexane.

**Coupling of the Diblock Macromonomer with Poly(\(\alpha\)-methylstyryl)lithium): The Formation of ABC Star Anion**

The resulting diblock macromonomer is used to couple with poly(\(\alpha\)-methylstyryl)lithium (P\(\alpha\)MStLi) through the reaction of polymer anion towards the residual double bond of DDPE moiety. P\(\alpha\)MStLi is chosen because it does not attack the ester group in the addition reaction with diphenylethylene (DPE) or in the cross initiation of butyl acrylates.36,39,40 P\(\alpha\)MStLi is prepared from polymerization of \(\alpha\)-methylstyrene initiated by sec-BuLi in
THF at -78 °C for 6 h. The resulting poly(a-methylstyryl)lithium solution is transferred into the solution of diblock macromonomer, PSDDPE-b-PtBuMA, for the subsequent coupling reaction. The applied diblock macromonomer is either terminated and purified (in batch approach) or carrying a poly(butyl methacrylyl) anion (in situ, in one-pot approach). Upon addition of PzMStLi, a dark-red color immediately appears, indicative of the formation of diphenylethyllithium moiety. The reaction completes within 3–4 h. The resulting 3-arm star species is analyzed by GPC. As shown in Figure 1, both one-pot and batch approaches show increase in molecular weight after coupling. A shoulder at low molecular weight side appears for both approaches, which may contain a number of species such as polystyrene, PzMSt and diblock macromonomer. However, these substances can be removed easily from the final product by cyclohexane washing.

**Polymerization of 4-Vinylpyridine as the Fourth Arm**

The resulting ABC star anion, with a diphenylethyllithium center, is an appropriate initiator for polymerization of 4-vinylpyridine. However, the reaction condition is very critical. In one-pot approach, although the existence of PtBuMA enolate anion would not cause side reaction such as attacking the double bond of DPE because of its weak nucleophilicity, the same anion can initiate the polymerization of 4-vinylpyridine at an appropriate temperature, 0 °C, as reported by Schulz et al. in the synthesis of PtBuMA-b-P4VP block copolymer in THF. This initiation ability would complicate the one-pot synthesis of the present ABCD-type star copolymers in that the polymerization of vinyl pyridine would be possibly initiated by both diphenylethyllithium center and PtBuMA enolate anion. Fortunately, it was reported that the crossover initiation of 4-VP by PtBuMA enolate anion did not occur at -78 °C in THF. Therefore, the polymerization of 4-vinylpyridine is conducted at -78 °C in THF/cyclohexane (4.3/1 v/v). The crossover initiation of 4-VP by diphenylethyllithium of the ABC star is indicated by the color change from dark red into orange. The polymerization is terminated with methanol. Surprisingly, the termination reaction lasts for 4–5 h during which the orange color slowly disappears.

In comparison of the GPC traces of ABC and ABCD star copolymers (lines d/d’ and e/e’ in Fig. 1), one can hardly see any shift in elution time for the latter in spite of the incorporation of P4VP segment as detected by NMR (vide infra). This implies that the hydrodynamic volumes of the two species are quite close to each other. In addition, both diagrams display the shoulder at lower molecular weight caused by those occasionally terminated and/or unreacted species in the coupling reaction. Therefore, the shoulder in the final product may contain diblock copolymer, PzMSt-b-P4VP, a byproduct by the initiation of residual PzMStLi, in addition to polystyrene, PzMSt and diblock macromonomer. Thus, the final reaction solution is precipitated from large amount of water. The obtained white powder is stirred with large amount of cyclohexane overnight. GPC traces of the crude and purified product are given in Figure 1 (III). The purification process is efficient as indicated by the disappearance of the GPC shoulder. On the GPC trace of the purified product, a broad peak at large molecular weight is observed and ascribed to micelle formation in the testing solvent, THF. The solution of ABCD product in THF before filtration for GPC exhibit blue opalescence. In

![Figure 2. 1H NMR spectra of (a) the monoadduct and (b) diblock macromonomer. (a) PS-DDPE after precipitation from methanol and vacuum drying; (b) Reaction mixture in the preparation of PSDDPE-b-PtBuMA in THF. The reaction conditions are identical to those in Figure 1.](image-url)
fact, the final reaction solutions for all polymerizations except run no. 1 in Table 1 exhibit blue opalescence, indicating micelle formation due to the amphiphilicity of the product. Besides, the same diagram displays a tailing effect, which is mainly due to the adsorption of P4VP segment to the GPC column whereas the contamination by PzMSt-b-P4VP diblock copolymers cannot be excluded.

A number of ABCD-type miktoarm star polymers with different arm lengths or compositions are synthesized, as summarized in Table 1. NMR has been used to determine the composition of various samples at different steps of the reactions. An example is given in Figure 3, with the assignment for the peaks at δ = 8.33 (−C6H4N of P4VP), 6.5–7.0 (−C6H5 of PS-DDPE, −C6H4N of P4VP), 1.12, 1.01 (−CH3 of PrBuMA), 0.36 (−CH3 of PzMSt). The composition is determined by the integration of various signals. With the GPC measured molecular weight of PS-DDPE and the composition, the molecular weights of PrBuMA and P4VP arms have been estimated (Table 1). Preliminary result of light scattering shows unusually larger molecular weight than the theoretical value and that in Table 1. The reason is not clear. Systematic investigation of the solution behavior of the products, together with the following hydrolyzed ones, will be carried out in the future.

Hydrolysis of (PS)(PrBuMA)(PzMSt)(P4VP) to Zwitterionic Star Copolymers

Hydrolysis

The 4-arm star copolymer is hydrolyzed with concentrated HCl solution in a mild condition as described by Stadler and Giebeler.24 The resulting carboxylic acid is evidenced by a broad band from 3300 to 2500 cm⁻¹ and slightly red shift of the band for carbonyl group absorbance to 1718 cm⁻¹, as shown in Figure 4. In addition, a double band at 1392 and 1367 cm⁻¹, characteristic of t-butyl (−(CH₃)₃) group, has disappeared after hydrolysis.

The hydrolyzed product is also analyzed by ¹H NMR in a mixed solvent of THF-d₈/D₂O. It is difficult to find a solvent or solvent mixture in which the hydrolyzed product forms clear solution. The solution in THF-d₈/D₂O is the clearest, yet with slight blue opalescence. Figure 5 shows the ¹H NMR spectra of the product before (line a) and after hydrolysis (line b). The signal at

<table>
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<th>Sample</th>
<th>Method</th>
<th>One-pot</th>
<th>Batch</th>
</tr>
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<tbody>
<tr>
<td>No.</td>
<td>No.</td>
<td>Mₙ,GPC (10⁶ Da)</td>
<td>Mₙ,NMR (10⁶ Da)</td>
</tr>
<tr>
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<td>4</td>
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<td>5</td>
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δ = 1.4 ppm for protons of t-butyl disappeared after hydrolysis. In addition, the signals between 6.2–7.2 ppm become fused due to the aggregation of the amphiphilic star copolymers in solution.

The hydrolyzed product possesses both anionic (carboxylic group) and cationic (pyridine group) segments that respond to change in pH. Figure 6 shows the results of potentiometric titration together with turbidity measurement. The two plateaus at pH ≈ 3.7 and 8.0 correspond to buffer zones of pyridium salt and carboxylic acid, while the two sharp transitions correspond to the complete deprotonation of pyridium and carboxylic acid groups, respectively. At the first transition (pH ≈ 6.2) the solution became turbid with the minimum transmittance, indicative of the isoelectric point (IEP) at which the polyampholyte was electrically neutral and usually insoluble. All these features are in agreement with those of diblock copolymer, PVP-b-PAA,22a and tertiary block copolymer, PS-b-PVP-b-PAA.24 It is noted, however, that the turbidity of the solution cannot be recovered totally from the minimum point when the solution become basic. This phenomenon is different from the turbidimetry of PVP-b-PAA22a during NaOH titration, and similar to that of PS-b-PVP-b-PAA,24 possibly due to stronger salt-out effect.

Figure 3. 1H NMR of the monoadduct (PS-DDPE), diblock macromonomer (PSDDPE-b-PtBuMA), 3-miktoarm star, and 4-miktoarm star copolymers (no. 3, Table 1) through one-pot process. The reaction conditions are identical to those in Figure 1 (I).

Figure 4. FTIR spectra of 4-miktoarm star copolymer (no. 3 in Table 1) before and after hydrolysis. Hydrolysis: copolymer: 0.11 g, HCl (concentrated): 0.6 mL, in 1,4-dioxane at 85 °C for 10 h.

Figure 5. 1H NMR spectra of 4-miktoarm star copolymer (no. 3 in Table 1) before and after hydrolysis under the same reaction condition as in Figure 4.

Figure 6. Potential titration (lower) and turbidimetry (upper) of the hydrolyzed product of 4-miktoarm star copolymer (no. 3 in Table 1). The reaction conditions are same with those in Figure 4.

effect (NaCl) for polymers with higher content of hydrophobic segments.

CONCLUSIONS

ABCD-type miktoarm star copolymers of styrene, α-methylstyrene, tert-butyl methacrylate, and 4-vinylpyridine were synthesized by either one-pot or batch anionic polymerizations using m-DDPE as the starting material. The polymerization sequence and the reaction media are very selective according to the activity of the propagating anion towards the double bond of DDPE moiety. The products were characterized by GPC, MALDI-TOF MS, and 1H-NMR. The subsequent hydrolysis of the product produces zwitterionic miktoarm star copolymers, which is soluble at lower pH but insoluble in neutral and basic solution. This is the first report on one-pot synthesis of ABCD-type star copolymers, and on zwitterionic star copolymers of the same topology. In addition, the methodology can be extended to the synthesis of other 4-arm such as ABC2, A2B2- and AB3-type copolymers with rational choices of monomers and polymerization sequences.

Nevertheless, the monomer choices for different arms are critical. The principle is as follows. The first arm can be made from hydrocarbon monomers such as styrene, α-methyl-styrene, isoprene, and butadiene. The selectivity of the second arm is limited to specific monomers such as butyl methacrylates, hexamethylcyclotrisiloxane (D3), ethylene oxide (EO), of which the propagating anion will not attack the remaining double bond of MDDPE. Another prerequisition for the second arm is that it should not carry functional groups that can be attacked by the living center of the third arm. The choice of the third arm depends on the reactivity of the corresponding propagating anion, which should be able to add to the remaining double bond of m-DDPE moiety while inert to the functionality of the second arm. PzMSt is chosen because it is stable to butyl methacrylate units. The suitable monomer for the last arm is that capable of being initiated by DPE anion, but stable to the presence of the living anion of the second arm. The propagating anion of the fourth arm should not attack the backbone of the second block. In addition, the maintenance of the stoichiometry is crucial. Any deviation from stoichiometry, either by feed error or anion neutralization, will cause formation of diblock and homopolymer byproducts. Therefore, the methodology can be used to synthesize a series of ABCD miktoarm star copolymers, but certainly with monomer limitation and possible byproduct contamination.

This work is subsidized by NSFC (20674008) and National Basic Research Program (2005CB623800). J. He and Y. Yang thank NSFC for the program of “Excellence in Research Groups” and “Excellence in doctoral dissertation of China”.

REFERENCES AND NOTES


